# H4: Derive Van't Hoff Equation

For binary system.

$$G = \Delta G = \Delta G^{id} + \Delta G^{ex} = RT\{\underset{x_A}{x}\ln x + \underset{x_B}{(1-x)}\ln(1-x)\} + \sum_{i=1}^{\infty}(A_i + B_i T)x^i$$

From Gibbs-Duhem eqn,

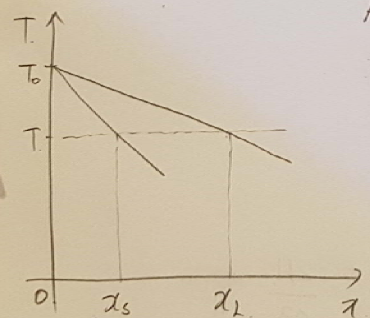
$$g_A = G - x\frac{dG}{dx} = RT\{x\ln x + (1-x)\ln(1-x)\} - x\,RT\{\ln x + \cancel{1} - \ln(1-x) - \cancel{1}\}$$

$$+ \sum_{i=1}^{\infty}(A_i + B_i T)x^i - \sum_{i=1}^{\infty}(A_i + B_i T)\,i\,x^i$$

$$= RT\ln(1-x) + \sum_{i=2}^{\infty}(1-i)(A_i + B_i T)x^i$$

$$= RT\left(-x - \frac{1}{2}x^2 - \frac{1}{12}x^3 - \cdots\right) + \sum_{i=2}^{\infty}(1-i)(A_i + B_i T)x^i$$

$$\simeq -RTx \quad (\text{for small } x)$$




At melting point $T_0$, $G_l = G_s \Rightarrow g_{A(l)} = g_{A(s)}$ $(x=0)$

If we change temperature slightly to T and if the equilibrium is to be maintained,

$$g_{A(s)} = g_{A(l)}$$

$$\Rightarrow -RT x_{A(s)} + (T_0 - T)S_{(s)} = -RT x_{A(l)} + (T_0 - T)S_{(l)}$$

$$RT(x_{A(l)} - x_{A(s)}) = (T_0 - T)\underbrace{(S_{(l)} - S_{(s)})}_{\Delta S}$$

$$\therefore \frac{x_{A(l)} - x_{A(s)}}{T_0 - T} = -\frac{(x_{A(l)} - x^{\circ}_{A(l)}) - (x_{A(s)} - x^{\circ}_{A(s)})}{T - T_0}$$

for $T \to T_0$, $$\left.\frac{d}{dT}(x_{A(l)} - x_{A(s)})\right|_{T=T_0} = -\frac{\Delta S}{RT_0} = -\frac{\Delta H}{RT_0^2}$$

# H4: Derive Van’t Hoff Equation

- We can use this equation for calculating how far the melting point will drop as the result of dissolving a small quantity of a substance

- We can use it without further knowledge of the binary system. All we need to know is the entropy of fusion(or heat of fusion) and the melting point of the pure component.

- This formula can be a simple way to check certain phase diagrams